SYNCHROTRON SMALL ANGLE X-RAY SCATTERING OF SLOW SPINODAL DECOMPOSITION IN A BLOCK COPOLYMER(Session III : Complex Fluids, The 1st Tohwa University International Meeting on Statistical Physics Theories, Experiments and Computer Simulations)

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Phase transitions of block copolymers have been an important and interesting topic in nonequilibrium statistical physics in recent years. Block copolymers exhibit microphase separation transition and form periodical microdomains. However, most of the studies have been concerned with the phase diagram and the equilibrium structure. Many papers[1-8] reported the experimental results for the ordering process of block copolymers. However, only two papers, by Connel and Richards[3] and by Stühn et al.,[8] compared the experimental results with the CHC theory[9,10]. However, they did not find the q-dependence of Onsager kinetic coefficient $\Lambda(q)$.

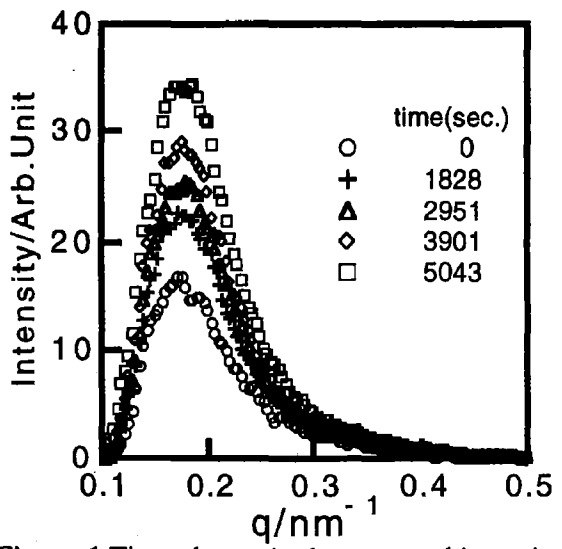

Figure 1 Time change in the scattered intensity as a function of q after a temperature jump from 23°C to 228°C.

The other papers reported that the ordering dynamics of block copolymer progresses via nucleation and growth because the systems were quenched near the order-disorder transition (ODT) point where the fluctuation effects played a very important role. Here we investigated the ordering dynamics in the block copolymer poly(styrene-*b*-*tert*-butylstyrene) quenched deeply by means of small-angle X-ray scattering (SAXS). A block copolymer poly(styrene-*b*-tert-butylstyrene) in the disorder state has been prepared by fast solution casting. The phase separation process induced by a temperature jump from the frozen disordered state at room temperature to above the glass transition temperature was investigated by using time-resolved synchrotron small-angle X-ray scattering. The scattered intensity grow with time at all observed q-region as shown in Fig.1. The exponential growth of the scattered intensity with time is found to continue up to 4.9×10^3 s and the early stage of the ordering in the block copolymer can be approximated by the Cahn linearized

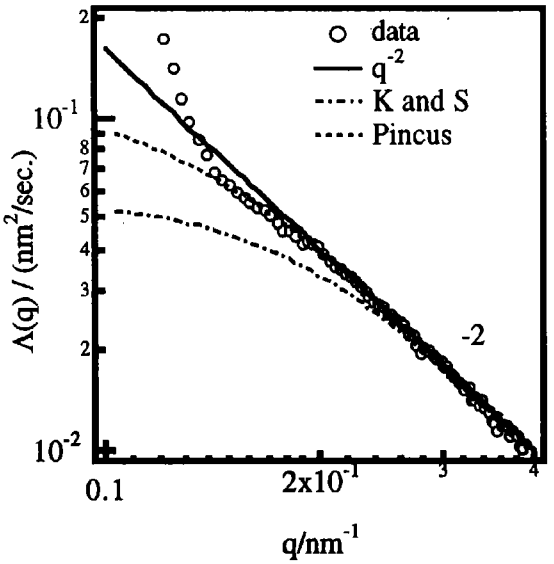

Figure 2 Onsager coefficient Λ(q) as a function of q. The solid line has a slope of -2. K and S, and Pincus denote Kawasaki and Sekimoto theory and Pincus theory, respectively.

theory[9], indicating that the phase separation occurred via spinodal decomposition. This is because the fluctuation effects are negligible at deep quench conditions. The value of R(q) and that of the χ parameter at the phase separation temperature, together with the q-dependence of Λ(q) are obtained by an analysis of the Cahn linearized theory. At $qR_{g,PS} >> 1$ and $qR_{g,PtBS} >> 1$, we found the q^{-2}-dependence in Λ(q) as predicted by Kawasaki and Sekimoto[9],where $R_{g,K}$ is the radius of gyration of the Kth component. The experimental results over the entire q-range, however, were inconsistent with the theoretical predictions as shown in Fig.2.

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